ORGANIC DEPOSITION IN PETROLEUM STORAGE TANKS AT REFINERIES DUE TO BLENDING OPERATIONS

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Received: 23.07.2019 / Revised: 25.10.2019 / Accepted: 25.10.2019 / Published on line: 20.12.2019

ABSTRACT

Petroleum blending is viewed as a critical optimization strategy adopted by several operations of petroleum production in the refineries around the world. A persistent problem called crude oil incompatibility occurs when the mixture of different oils lead to the formation of solid phases due to the precipitation of asphaltenes. The present work investigates the relationship between the occurrence of sludge in petroleum storage tanks and petroleum blending operations. Hildebrand solubility parameters of the oils were determined, revealing that one of the samples of petroleum analyzed is at the threshold of the asphaltene flocculation parameter, with an average of 16.1 Mpa$^{1/2}$. Thus, it implies that blending operations with dissimilar petroleum feedstocks must be well planned, since they can initiate the precipitation of the asphaltenes and, consequently, the formation of sludge that accumulate and deposit as sediments inside petroleum storage tanks.

KEYWORDS
compatibility of crude oil; organic deposition; solubility parameter

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doi:10.5419/bjpg2019-0022
1. **INTRODUCTION**

Petroleum is a naturally occurring fluid consisting essentially of hydrocarbons. Likewise, a great variety of oils with differing composition and physical properties can be found on the Earth’s surface.

Based on the chromatographic analysis, it is possible to perform the separation and classification of petroleum in saturate (S), aromatic (A), resins (R), and asphaltenes (A) (Ashoori et al., 2017; Fingas, 2015; Aske et al., 2001).

Different atoms of carbon and hydrogen are present in the oils at lower concentrations. Smaller species are spread within the various fractions through functional groups of acid/basic or metallic complexes. Several studies have shown that these groups are concentrated mainly on the chemical structure of petroleum's heavy fractions, notably asphaltenes and resins (Castilho & Vargas, 2016; Chilingarian & Yen, 2009; Speight, 1994).

Asphaltenes and resins are petroleum fractions with high molar masses. They present a chemical structure that consists of one or more polycondensed aromatic rings, has lateral aliphatic chains, and contains oxygenated, nitrogenous, sulfuric, and metal groups (Speight, 2014; Gafanova & Yarranton, 2001; Leon et al., 2000). These fractions differ by size and behavior, despite of their chemical similarity.

Asphaltenes are, relatively, the compounds with higher polarity and aromaticity of oils (Shadman et al., 2017; Ferreira et al., 2016; Honse et al., 2012).

In an attempt to explain many operational problems, three aspects related to asphaltenes and resins are emphasized in the scientific literature:

(i) The complex chemical structure and concentration of atoms other than carbon and hydrogen;
(ii) The interfacial and colloidal behavior (Langevin & Argillier, 2016; Mousavi et al., 2016; Guzmán et al., 2017);
(iii) The role of asphaltenes in the petroleum physical structure (Chen et al., 2015).

Among the operational problems related to the asphaltene fractions (asphaltenes and resins), the most important are: the formation of deposits in the stages of production; the stabilization of emulsions; and the reversal of wettability.

Organic deposition is the main negative aspect of asphaltenes. Depending on the extent to which it occurs, the formation of deposits can lead to great losses, making the operation totally unfeasible (Santos et al., 2017; Chen et al., 2012).

Variations in temperature, pressure, and chemical composition may precipitate asphaltenes, affecting negatively all stages of production (Hasanvand et al., 2015; Goual, 2012). Deposition may result in total or partial blockage of the flow in reservoirs, production columns, and drainage ducts. It can also damage a variety of equipment and form sludge inside the oil storage tanks.

The cost associated with asphaltene deposition during production and refining operations is estimate in billions of dollars per year, and, for this reason, the prevention or minimization of asphaltene precipitation is an important goal for the oil companies (Rogel et al., 2010; Anderson & Speight, 1999). The negative economic effect of asphaltene deposition also includes the expenses associated to petroleum sludge removal and disposal, being the latter the highest one (Johnson & Affam, 2019).

There is still no sustainable description of the aggregation mechanisms to explain the destabilization of asphaltenes. In this sense, this issue is the subject of ongoing investigations.

An important property associated with asphaltenes and the solvent medium (oil) for describing the precipitation is the Hildebrand solubility parameter. Theoretical developments have allowed a prediction of the onset of asphaltene precipitation by the adding a flocculant agent to the petroleum (Mitchell & Speight, 1973), or blending crude oils (Ramos et al., 2013).

Blends using crude oils of distinct compositions may be incompatible, resulting in the consequent precipitation of asphaltenes (Wiehe, 2008). Under unfavorable conditions, asphaltenes tend to self-associate into small nano-aggregates that can grow into larger aggregates and, eventually, flocculate and precipitate (Chrisman et al., 2012; Trejo & Ancheyta, 2007).
Several factors may alter the phase equilibrium of the petroleum leading to the formation of solids, either by the precipitation of asphaltenes, resins, paraffins, or others (Speight, 1998). In many cases, the solids formed are called sludge and are composed of a material with difficult experimental characterization (Speight, 2014).

This work evaluates the potential for sludge formation due to the precipitation of asphaltenes by the mixture of crude oils. It simulates refinery feedstock operations from the measurements of the onset of asphaltene precipitation and the calculations of the crude oils solubility parameters. The aim is to identify relationships between the blending operations that can justify the large accumulation of sludge and contribute with operational programs that can reduce the amount of sludge formed at the refineries.

2. MATERIALS AND METHODS

2.1 Materials

Two different petroleum samples (identified as Petroleum "A" and Petroleum "B") were used to develop the work and to perform the laboratory analyses, both from a given refinery. Also, a sample named Petroleum "C" was used as the reference petroleum. Sludge samples, of pasty consistency, were collected from the bottom of the petroleum storage tank. Solvents n-heptane (C$_7$H$_{16}$) and toluene (C$_6$H$_5$CH$_3$) both with analytical purity were used.

2.2 Methodology of the onset of asphaltene precipitation by optical microscopy

The identification of asphaltene precipitation was observed using an optical microscope. The experimental procedure consists of adding a flocculant (n-heptane) to the petroleum, in successive aliquots and, later, inspecting it with the microscope. At each addition of the flocculant, a small portion of the sample is inserted into a microscope slide, and analyzed visually on the optical microscope until the formation of dark spots in the form of fractals, characterizing the onset of asphaltenes precipitation.

The relationship between the minimum amount of flocculant and the petroleum mass represents the onset of asphaltene precipitation (OP) expressed according to Equation 1.

$$\text{OP} = \frac{\text{volume of flocculant (mL)}}{\text{petroleum mass (g)}}$$  

(1)

2.3 Determination of the Hildebrand solubility parameter of petroleum

The procedure for determining the Hildebrand solubility parameter of the crude oils was based on the work of Ramos et al. (2013) applying the crude oils precipitation onset and taking as reference the value of 16.2 Mpa$^{1/2}$ for the asphaltene flocculation parameter and the value of 15.3 Mpa$^{1/2}$ for solubility parameter of the solvent used, in this case the n-heptane.

The solubility parameters of the crude oil under analysis were calculated by Equations (2) or (3).

$$\delta_f = \delta_p \times \theta_p + \delta_s \times \theta_s$$  

(2)

Where:

- ($\delta_f$) is the asphaltene flocculation parameter;
- ($\delta_p$) is the petroleum solubility parameter;
- ($\theta_p$) is the volumetric fraction of petroleum at the precipitation onset;
- ($\delta_s$) is the solvent solubility parameter; and
- ($\theta_s$) is the volumetric fraction of the solvent at the precipitation onset.

$$\delta_f = \delta_p \times \theta_p + \delta_s \times \theta_s + \delta_{PR} \times \theta_{PR}$$  

(3)

In Equation 3:

- ($\delta_{PR}$) is the solubility parameter of the reference petroleum;
- and ($\theta_{PR}$) is the volume of petroleum used for starting precipitation reference.

2.4 Methodology used for qualitative characterization of the particulate material (sludge)

Sludge samples were submitted to a centrifugation process to promote phase separation at different densities. To determine the nature of the particles, the oily sludge sample was
inspected under an optical microscope through a polarizing lens. This procedure is useful for characterizing crystalline and amorphous substances, wherein the polarizing filter promotes only the selection of a vibration plane of light waves, resulting in the polarized light plane with the birefringent macromolecular components, which have brightness while no birefringents have a dark background.

3. RESULTS AND DISCUSSIONS

3.1 Petroleum "A" and Petroleum "B" result analyses

For Petroleum A the precipitation onset was determined with the addition of n-heptane. The experiments were conducted at the temperature of 20°C following the procedure described in section 2.2.

The precipitation onset assumes the least amount of heptane necessary for the appearance of the asphaltene particles (Wang & Buckley, 2001), as exemplified in Figure 1(a). These particles were identified visually with the aid of the optical microscope through the occurrence of dark spots of fractal and amorphous aspect (when submitted to a polarizing lens). Figure 1 shows two images from the precipitation of asphaltenes in petroleum A. The onset of asphaltene precipitation (OP) is not always easy to determine, depending especially on the technique applied and the petroleum characteristics (asphaltene content and particle size). Figure 1(b) was obtained in a condition above OP, in which the particles become more visible under the microscope, due to size and/or quantity, assisting in the confirmation of the first critical event.

In Figure 1(b), due to the greater presence of flocculant in the petroleum, the particles of asphaltenes appear larger, making it easier to confirm the critical event.

For petroleum A the onset precipitation obtained was 4.7 mL/g and it represents the average of three independent experiments, as shown in Table 1. Its Hildebrand solubility parameter was calculated applying Equation 2 with the corresponding OP value.

The solubility parameter may be indicative of petroleum stability, as already pointed out in the works of Ramos et al. (2013); Haji-Akbarit et al. (2013); and Mutelet et al. (2004). In this case, the solubility parameter resulted in a value of 19.9 MPa$^{1/2}$, very close to the solubility parameter of toluene (18.3 MPa$^{1/2}$), which is known to be a good solvent for asphaltenes. This result indicates that the conditions favor the maintenance of asphaltenes in the solution.

Applying the same procedure used in petroleum A, it was not possible to determine the onset of...
asphaltenes precipitation in petroleum B. Successive additions of heptane and inspections were made in the optical microscope, but the formation of solid phases consistent with the precipitation of asphaltenes was not observed. This impossibility can have two main causes: (i) the fact that some crude oils have large amounts of suspended particles, which makes it difficult to visualize asphaltenes, or (ii) the fact that crude oils have low asphaltene content (Ramos et al., 2013).

In this work, the second alternative (low asphaltene content) was verified, since petroleum B composition data showed that the asphaltene content is 0.1% (m/m), according to the supplier’s record.

With the objective of calculating the Hildebrand solubility parameter of petroleum B, we mixed petroleum B with the reference petroleum and, thus, determining the OP in the blend. Subsequently, the result was applied in Equation 3 to determine the solubility parameter.

The reference petroleum was chosen because it contains necessary characteristics, such as the absence of suspended particles, and it allows a precise determination of the asphaltenes OP. The reference petroleum OP obtained was 4.7 mL/g in three independent experiments.

In the blend of 50% by mass between petroleum B and reference petroleum, no occurrence of particles was observed (Figure 2). Thus, one can conclude that, in this proportion, the blend is compatible.

In the crude oils blend, the onset of asphaltenes precipitation was 2.3 mL/g. The precipitation was quite evident as one can see in Figure 3 by looking at the dark spots in contrast to the image background.

The OP results in the petroleum blend are shown in Table 2 for three replicates, as well as the petroleum B Hildebrand solubility parameter.

Table 2 shows the average value of 16.1 MPa$^{1/2}$ of the Petroleum B Solubility Parameter, very close to the asphaltenes flocculation parameter (16.2 MPa$^{1/2}$), as shown in Figure 4. This result, below the limit of the asphaltenes flocculation parameter, means a greater susceptibility of asphaltenes
precipitation in this petroleum, with implications in the blending operations at the refineries (Wiehe & Kennedy, 2000).

Results of petroleum A and B solubility parameters shows that care must be taken in blending operations between crude oils. The petroleum from the tank (petroleum B) is at saturation condition and, as its volume is greater than that of the added petroleum (petroleum A); it may occur that the medium acts in the flocculation of asphaltenes present in petroleum B. These results may explain the formation of sludge that builds up in the tank over time.

3.2 Analysis of the sludge collected at the tank’s bottom

To establish a relationship between asphaltene precipitation due to the blending operations between the petroleum feedstock and the tank petroleum, qualitative aspects of the sludge from the tanks were investigated.

Initially, a centrifugation was performed to separate the solids from the supernatant oil. As a result of the centrifugation process, it was possible to separate the sludge into two parts, one solid and other liquid (supernatant).

The supernatant phase, after resting for 24 h, was separated into two new liquid phases, as shown in Figure 5 (5a - supernatant and 5b - supernatant with two liquid phases).

Therefore, we could observe that the sludge is composed by at least three distinct phases, one solid and two other liquid with distinct specific mass.

Thus, it was possible to assume that the solid material of the sludge promotes its stabilization, and that, after its removal, it is possible to observe the separation of phases. Such behavior is consistent with the stabilization of emulsions in the petroleum industry, in which finely divided solids or natural surfactants of the crude oils (asphaltenes and resins) can act at the interface between two liquids to stabilize the system.

| Blend of petroleum B and reference petroleum | | |
| Experiment | OP (mL/g) | δ MPa$^{1/2}$ |
| 1 | 2.3 | 16.1 |
| 2 | 2.3 | 16.1 |
| 3 | 2.4 | 16.2 |
| Average | 2.3 | 16.1 |

Table 2. Onset of asphaltenes precipitation (OP mL/g) of the blend between petroleum B and reference petroleum in the proportion of 50% by weight and the respective solubility parameters (δ MPa$^{1/2}$).

Figure 4. Graph with values of the petroleum A and petroleum B solubility parameter and the delimitation of the asphaltenes flocculation limit.
This proposal was evaluated through the microscopic analysis of the supernatant. The presence of emulsions between two liquid phases and the occurrence of asphaltene-like particles was confirmed (Figure 6).

However, the birefringence phenomenon was observed in the supernatant obtained when subjected to a polarizing lens (Figure 6b), indicating that the particles could be amorphous (as asphaltenes and resins) and crystalline in nature (like paraffins and inorganic solids).

To infer about the nature of the suspended particles, the solid sludge was also investigated in a polarizing lens (Figure 7). The manifestation of black/dark spots that fill most of the slide can be observed. This phenomenon is accepted as being the asphaltenes or other materials originating from crude oil. Bright spots may also be observed indicating the presence of crystals which may originate from petroleum or from other phases, possibly inorganic solids assuming that the other phase present in the system is aqueous.

The fact that asphaltene particles are a predominant part of the sludge indicates that the supernatant petroleum is saturated in asphaltenes, and hence the petroleum solubility parameter of
the tank (supernatant + sludge) must have a solubility parameter close to the asphaltenes flocculation parameter. Thus, the blend between the less soluble petroleum with the tank petroleum (which is saturated) can result in the precipitation of asphaltenes, contributing to the increase of sludge formation.

4. CONCLUSIONS

The methodology for the experimental determination and calculation of Hildebrand solubility parameters was applied to the crude oils used in this work. The results obtained were 19.8 Mpa$^{1/2}$ for petroleum A and 16.1 Mpa$^{1/2}$ for petroleum B. Based on the analysis of these parameters, one can establish that petroleum B has a great potential to precipitate asphaltenes and to increase the amount of sludge.

It was also found that the sludge is predominantly formed from asphaltenes particles and that the sludge from the tank is composed by a petroleum phase, a particulate material phase, and an aqueous phase.

Due to the blending operations of crude oil feedstock with low solubility parameters, such as those of petroleum B, the formation and increase of sludge in the storage tank can occur substantially.

5. REFERENCES


